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# Laboratory Processing and Characterization of Waste Materials From Manganese Nodules

By Benjamin W. Haynes, David C. Barron, Gary W. Kramer,  
Riki Maeda, and Michael J. Magyar



UNITED STATES DEPARTMENT OF THE INTERIOR



**Report of Investigations 8938**

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**UNITED STATES DEPARTMENT OF THE INTERIOR  
William P. Clark, Secretary**

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**UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT**

atm	atmosphere	$\mu\text{m}$	micrometer
cm/s	centimeter per second	mL	milliliter
$^{\circ}\text{C}$	degree Celsius	mL/g	milliliter per gram
g	gram	mV	millivolt
gal	gallon	min	minute
g/L	gram per liter	ng/g	nanogram per gram
h	hour	ppm	parts per million
in	inch	pct	percent
kg	kilogram	pg/g	picogram per gram
L	liter	pcf	pound per cubic foot
lb	pound	psi	pound per square inch
L/min	liter per minute	psig	pound per square inch, gauge
$\mu\text{g/g}$	microgram per gram	wt pct	weight percent
$\mu\text{g/mL}$	microgram per milliliter		

# LABORATORY PROCESSING AND CHARACTERIZATION OF WASTE MATERIALS FROM MANGANESE NODULES

By Benjamin W. Haynes,<sup>1</sup> David C. Barron,<sup>2</sup> Gary W. Kramer,<sup>2</sup>  
Riki Maeda,<sup>3</sup> and Michael J. Magyar<sup>3</sup>

## ABSTRACT

This Bureau of Mines report describes the laboratory processing of manganese nodules and the results of tailings characterization obtained during the cooperative program with the Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and the Bureau. Five technically feasible first-generation nodule processing methods were operated at bench scale to generate sufficient tailings and slags for physical and chemical analyses. A description is given for the laboratory operation of the individual unit operations of each process.

The laboratory-generated tailings and slags were tested for physical properties, mineral content, elemental and ion content, and leachability for all five processes. The results of leachate testing using the Environmental Protection Agency extraction procedure (EP) toxicity test, the American Society for Testing and Materials shake extraction test, and the EPA-U.S. Army Corps of Engineers seawater elutriant test showed very low to negligible leaching of metals from the tailings and slags. Results of the EP toxicity test demonstrated that the wastes are nonhazardous as defined in the Resource Conservation and Recovery Act (Public Law 94-580).

## INTRODUCTION

Deep seabed mining for manganese nodules, including the processing of nodules to recover value metals, raises a variety of environmental, social, and economic considerations. To address the waste management aspects of the recovery of value metals from nodules, the National Oceanic and Atmospheric Administration (NOAA) of the Department of Commerce, the Environmental Protection Agency (EPA), and the Department of the Interior's Bureau of Mines and Fish and Wildlife Service, after consultation with affected and concerned interests, embarked on a multiyear cooperative research program that had as its overall objective:

"To provide information needed by Federal and State agencies in preparation for receipt of industry's commercial waste management plans."

Under the Deep Seabed Hard Mineral Resources Act of 1980 (Public Law 96-283), NOAA was designated as the lead agency in developing terms, conditions, and restrictions for the proposed mining of nodules and for the disposal of wastes. The NOAA-funded research conducted by the Bureau of Mines was entitled, "Analysis and Characterization of Manganese Nodule Processing Re-

jects," and had the objective of obtaining a first-order chemical and physical characterization of rejects from the types of manganese nodule processing techniques representative of those being developed by industry. This report is the fifth in a series of Bureau reports (1-4)<sup>4</sup> that can be used by (a) industry and environmental scientists in subsequent research to assess the potential effects of waste management alternatives and (b) regulatory agencies in the determination of the standards and test requirements to be met.

Four previous Bureau reports address the various aspects of the objective to obtain a first-order characterization of waste materials from processing nodules. One of the reports describes the mineralogical and elemental characteristics of Pacific Ocean manganese nodules (3), providing important knowledge of the processing feed material. A second report (4) details the five most technically feasible process flowsheets for first-generation plants. Reference 4 is based on a previous report (5) and contains updated and improved operating parameters for the five processes duplicated in the laboratory. A third report (2) uses information on nodule composition (3) and processing methods (4-5) to predict the compositions of the

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<sup>4</sup> Italic numbers in parentheses refer to items in the list of references at the end of this report.

tailings generated by each of the processes. The fourth report (1) details methods for physical and chemical analyses of nodules and tailings.

Of the many processes potentially available for the recovery of value metals (Co, Cu, Mn, Mo, and Ni) from manganese nodules, only five are considered at present to be technically feasible for first-generation nodule processing (4-5). These processes are as follows:

1. Gas reduction and ammoniacal leach.
2. Cuprion ammoniacal leach.
3. High-temperature and high-pressure sulfuric acid leach.
4. Reduction and hydrochloric acid leach.
5. Smelting and sulfuric acid leach.

The two ammoniacal leach processes and the high-temperature and high-pressure sulfuric acid process are designed to recover three metals (Co, Cu, and Ni) with some possible recovery of Mo. These are called three-metal processes although some manganese could be recovered

from the tailings if required. In this research, no attempt was made to recover manganese from the tailings of the three-metal processes. The remaining two processes, hydrochloric acid leach and smelting and sulfuric acid leach are designed to recover four metals (Co, Cu, Mn, and Ni) and are called four-metal processes. Manganese is recovered as either electrolytic manganese (HCl process) or as ferromanganese (smelting process). All five of these processes were operated on a bench scale modeled after the flowsheets (4-5) to generate sufficient tailings (rejects) for physical and chemical characterization.

The tailings were characterized physically, chemically, and mineralogically (1, 6-8) and were also subjected to three leachate tests: the EPA extraction procedure (EP) toxicity test (9); the American Society for Testing and Materials (ASTM) shake extraction test (10); and the EPA-U.S. Army Corps of Engineers (COE) seawater elutriant test (11).

## ACKNOWLEDGEMENTS

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standards, and manuscript reviews; Ocean Mining Associates for manganese nodule standards, samples, and manuscript reviews; and Ocean Management, Inc., for manuscript reviews.

## CHARACTERIZATION METHODS

The tailings generated in the laboratory-scale processes were subjected to a variety of analyses. After sufficient quantities of the tailings were generated, the tailings were washed to remove soluble metals and were blended. These tailings (~25 lb solids plus the accompanying liquids) were characterized for physical properties, chemical composition, mineralogical composition, and leachability.

The physical properties were determined using the standard soil mechanics tests (12-13) listed in table 1. All physical testing was performed at the Bureau's Spokane (WA) Research Center.

Elemental composition of tailings (liquid and solid phases) was determined by atomic absorption spectrophotometry using flame and electrothermal atomization

methods (1). The primary elements of interest are those elements on the Toxic Substance Control Act list of priority pollutants, the Resource Conservation and Recovery Act list of leachable metals for EP toxicity, and/or major and minor elements of economic importance. These elements are Ag, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, and Zn. Elements such as Al, Ca, K, Mg, Si, Ti, V, and others were determined to complete the tailings composition. Ionic species, primarily anions, were determined in both accompanying liquid and the solid phases of the tailings by ion chromatography (1, 14). The ionic species are ammonium, carbonate, chloride, fluoride, nitrate, phosphate, and sulfate. Other parameters such as pH were determined by standard laboratory methods (1). Mineralogical composition was determined on dried samples of tailings by X-ray diffraction and optical microscopy (1).

The tailings were tested with three leachate tests as stated earlier (9-11). The EP toxicity test and the ASTM shake extraction test are different methods for assessing the potential leaching properties of materials that may be used as landfill or impounded in tailings ponds. The EPA-COE seawater elutriant test designed for evaluating dredged material for ocean disposal, gives an indication of whether significant leaching of metals would occur in a marine environment if tailings were disposed of by ocean dumping or ocean outfall.

The results obtained from all analyses are given in the "Tailings Characterization" section. Detailed descriptions of the analyses methods are given in a previous report (1).

**Table 1.—Physical property testing for manganese nodule tailings**

Property	Procedure (12)
Grain size distributions:	
Plus 200 mesh .....	ASTM D422-63
Minus 200 mesh .....	Allen (13) <sup>1</sup>
Specific gravity .....	ASTM D854-58
Triaxial shear .....	ASTM D2850-70
Permeability .....	ASTM D2434-68
Density:	
Maximum .....	ASTM D698-78
Minimum .....	ASTM D2049-60
Atterberg limits:	
Liquid .....	ASTM D423-66
Plastic .....	ASTM D424-59
Soil class .....	ASTM D2487-69
Slurry density .....	ASTM D2216-71

<sup>1</sup> Using Bureau of Reclamation Earth Manual Procedure E13.

## MANGANESE NODULE FEED PREPARATION

Approximately 1 ton of Pacific manganese nodules and fragments recovered from the area of prime commercial interest, the Clarion-Clipperton fracture zone area (CC-zone area) as shown in figure 1, was used as the bulk feed material for all five processes. Earlier work (3) summarized the overall content of Pacific nodules from this and other areas of the Pacific. These summary values are shown in table 2. The nodules were received wet in four 55-gal drums. The contents of the four drums were spread on heavy Kraft<sup>5</sup> paper and allowed to air dry for approximately 3 days. The air-dried manganese nodules were crushed to minus 0.25 in. in a jaw crusher and then oven dried at 90° C for approximately 18 h. The cooled oven-dried minus 0.25-in material was further reduced to minus 80 mesh in a Braun pulverizer. The resulting minus 80-mesh material was blended for 4 h in a P-K twin shell V-blender in 200-lb lots. Three samples of each of six blends were analyzed for elemental content and the blended batches were compared to test homogeneity. Typical results of the elemental analysis for the batches are given in table 3. To ensure within-process feed homogeneity, small (20- to 30-lb) batches were rebled in a small twin-shell V-blender and analyzed prior to use

<sup>5</sup> Reference to specific products does not imply endorsement by the Bureau of Mines.

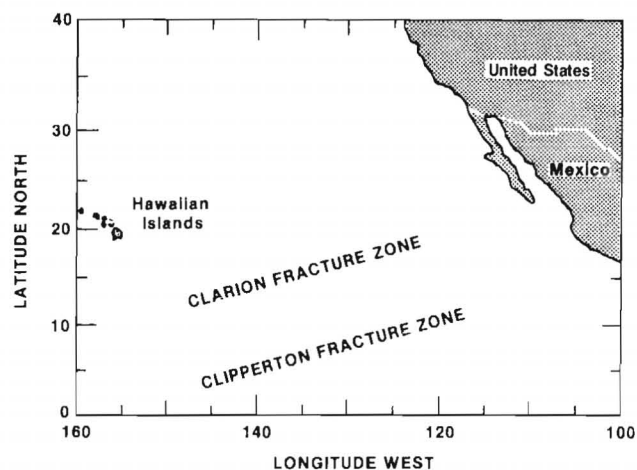


Figure 1. — Area of prime interest for first-generation manganese nodule mining, Clarion-Clipperton Fracture Zone.

in the laboratory process systems. The elemental analysis obtained on these small rebled batches did not vary significantly from the original analyses, and it was used in calculating percent solubilization.

Table 2.—Composition of CC-zone area Pacific manganese nodules, micrograms per gram (unless otherwise noted)

Element	Mean	Median	Element	Mean	Median	Element	Mean	Median
Ag .....ng/g.	101	39	Ge .....ng/g.	42	37	Re .....ng/g.	0.2	Ins
Al .....pct.	2.9	2.5-3.0	Hf .....ng/g.	6	5	Ru .....ng/g.	18	Ins
As .....ng/g.	159	164	Hg .....ng/g.	152	85	S (SO <sub>4</sub> ) .....pct.	1.84	0.40
Au .....ng/g.	1.93	1.92	Ho .....ng/g.	4	4	Sb .....ng/g.	37	36
B .....ng/g.	273	221	I .....ng/g.	510	230	Sc .....ng/g.	10	10
Ba .....pct.	0.277	0.200-0.220	Ir .....ng/g.	9.1	4.3	Se .....ng/g.	52	53
Be .....pct.	4	2	K .....pct.	1.01	0.80-0.90	Si .....pct.	7.6	6.0-6.5
Bi .....pct.	21	23	La .....pct.	157	130	Sm .....pct.	35	32
Br .....pct.	500	500	Li .....pct.	160	100	Sn .....pct.	108	80
C (CO <sub>3</sub> ) .....pct.	0.18	0.19	Lu .....pct.	1.8	2	Sr .....pct.	450	400-500
Ca .....pct.	1.7	1.5-2.0	Mg .....pct.	1.65	1.50-1.75	Ta .....pct.	11	11
Cd .....pct.	12.3	10-15	Mn .....pct.	25.4	26-27	Tb .....pct.	5.4	5
Ce .....pct.	532	340	Mo .....pct.	520	500-600	Te .....pct.	216	214
Cl .....pct.	0.53	0.78	N (NO <sub>3</sub> ) .....pct.	560	400	Th .....pct.	28	21
Co .....pct.	0.24	0.20-0.30	Na .....pct.	2.79	2.00-2.25	Ti .....pct.	0.53	0.40-0.50
Cr .....pct.	27	15-20	Nb .....pct.	74	80	Tl .....pct.	169	160
Cs .....pct.	0.75	<0.7	Nd .....pct.	158	141	Tm .....pct.	2.3	2
Cu .....pct.	1.02	1.00-1.10	Ni .....pct.	1.28	1.30-1.40	U .....pct.	6.8	5
Dy .....pct.	31	32	P (P <sub>2</sub> O <sub>5</sub> ) .....pct.	2,300	2,100	V .....pct.	470	400-500
Er .....pct.	18	19	Pb .....pct.	450	400-500	W .....pct.	76	80
Eu .....pct.	8	7	Pd .....ng/g.	6.2	6.3	Y .....pct.	133	111
F .....pct.	130	<100	Pr .....ng/g.	36	34	Yb .....pct.	20	17
Fe .....pct.	6.9	6-7	Pt .....ng/g.	97	110	Zn .....pct.	0.14	0.10-0.15
Ga .....pct.	11	6	Ra .....pg/g.	8.5	5.1	Zr .....pct.	350	350-400
Gd .....pct.	32	33	Rb .....pct.	15	15			

Ins Insufficient data for median.

Table 3.—Homogeneity of blended manganese nodule feed material, weight percent

Element	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Average	Element	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Average
Al .....%	2.52	2.61	2.50	2.42	2.50	2.59	2.52	Mg .....%	1.86	1.84	1.87	1.90	1.93	1.88	1.88
As .....%	.0055	.0073	.0054	.0076	.0067	.0079	.0067	Mn .....%	29.6	28.7	29.5	30.3	29.8	30.1	29.7
Ba .....%	.22	.17	.20	.31	.24	.22	.23	Mo .....%	.12	.11	.11	.12	.12	.11	.12
Be .....%	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	Ni .....%	1.34	1.30	1.33	1.35	1.34	1.31	1.33
Ca .....%	1.21	1.21	1.27	1.35	1.27	1.40	1.28	Pb .....%	.043	.041	.042	.039	.044	.043	.042
Cd .....%	.0017	.0017	.0017	.0018	.0018	.0018	.0018	Sb .....%	.0047	.0048	.0044	.0052	.0050	.0069	.0052
Co .....%	.23	.22	.23	.23	.23	.24	.23	Ti .....%	.16	.17	.16	.20	.16	.22	.18
Cr .....%	.002	.002	.002	.002	.002	.002	.002	Tl .....%	.020	.020	.020	.020	.020	.020	.020
Cu .....%	1.21	1.16	1.19	1.23	1.21	1.18	1.20	V .....%	.044	.043	.049	.045	.041	.045	.044
Fe .....%	5.56	5.37	5.43	5.38	5.44	5.55	5.46	Zn .....%	15	14	15	15	16	15	15
K .....%	1.00	.97	.93	.93	.91	.90	.94								

## LABORATORY PROCESSING

The actual laboratory conditions are presented, followed by results of analyses for the five processes in the next section. The objective of the laboratory processing studies was to generate sufficient tailings for chemical and physical characterization. Therefore, no further processing after the tailings washing or final slag generations was performed in the laboratory. The pregnant liquor or slag was sampled for analysis on each run to ensure adequate value metal extraction. Each unit operation performed in the laboratory is discussed and laboratory results reported. The results of all the process tailings analyses are presented together in the "Tailings Characterization" section to enable comparison of the process tailings. Overall summary process descriptions are given in reference 4.

### GAS REDUCTION AND AMMONIACAL LEACH PROCESS

The gas reduction and ammoniacal leach process is analogous to the Caron process (15) used on nickeliferous laterites at Nicaro, Cuba (16), and Greenvale, Australia (17). The primary differences between the Caron process practice and the manganese nodule process are in the methods of metal separation and purification. The reduction and leaching operations are direct applications of the Caron process. Flowsheets and descriptions of this process are given in reference 4.

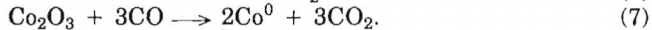
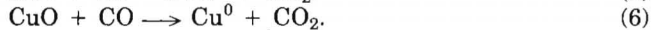
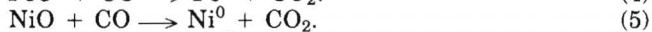
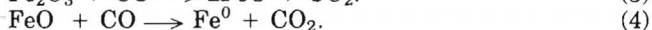
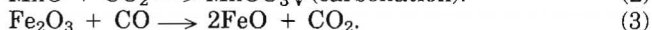
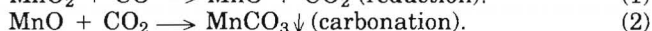
A comparison between laboratory operating parameters and those suggested for the proposed commercial process (4-5) is given in table 4 for those unit operations performed in the laboratory. A complete list of proposed commercial parameters is available elsewhere (4).

**Table 4.—Comparison of operating parameters and results for the gas reduction and ammoniacal leach process**

Parameter and unit	Proposed commercial	Actual laboratory
<b>REDUCTION</b>		
Reduction temperature .....°C.	625	625
Cooling temperature.....°C.	125	100
Mn reduction.....pct.	98	96.2 ± 3.4
<b>LEACHING-AERATION</b>		
Leachate composition, g/L:		
NH <sub>3</sub> .....	100	100
CO <sub>2</sub> .....	50	50
Temperature .....	40	40-50
Pressure..... atm.	1	1
Solubilization, pct:		
Co .....	70	51
Cu .....	90	87
Fe.....	~1	<1
Mn .....	~1	<2
Ni.....	90	65
Time per stage .....	1	1
Number of stages.....	3	4
<b>SOLID-LIQUID SEPARATION</b>		
Slurry density .....	35-40	29.4
Wash ratio .....	2	2
Wash liquid composition, g/L:		
NH <sub>3</sub> .....	100	100
CO <sub>2</sub> .....	50	50
Number of stages.....	4	4

### Reduction and Quenching

The objective of the reduction and quenching operation is to disrupt the manganese nodule crystal structure of MnO<sub>2</sub> by reducing Mn<sup>4+</sup> to Mn<sup>2+</sup> and to release the lattice-bound Co, Cu, and Ni for reduction and solubilization. By reducing the Mn<sup>4+</sup> to Mn<sup>2+</sup>, the structure of the primary manganese minerals of todorokite, birnessite, and/or vernadite (3) are altered and the desired leaching agent is able to solubilize the value metals. Quenching prevents reoxidation of Mn<sup>2+</sup> and facilitates the carbonation of the reduced manganese to form MnCO<sub>3</sub>. The following are the principal chemical reactions that occur during reduction:



Reaction 1 is the disruption of the MnO<sub>2</sub> structure allowing subsequent reduction of Ni, Cu, and Co (reactions 5, 6, 7, 8) and the carbonation of reduced manganese (reaction 2). Iron is also reduced to either the Fe<sup>2+</sup> state and/or possibly to the Fe<sup>0</sup> neutral state (reactions 3 and 4). It is desirable to reduce the iron only to the Fe<sup>2+</sup> state because iron reduced to the Fe<sup>0</sup> state may alloy with nickel metal. This formation of FeNi alloy retards and often prevents rapid solubilization of the nickel values associated with the alloy formation.

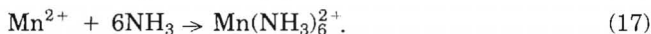
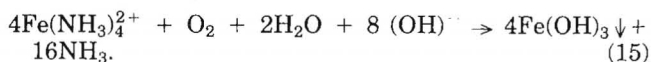
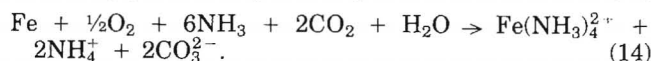
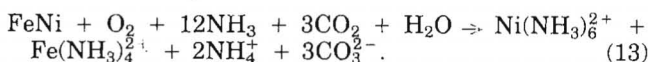
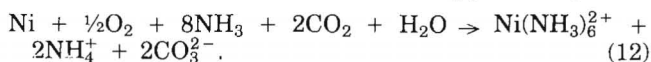
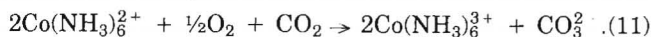
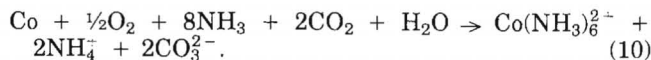
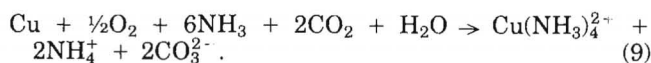
The laboratory reduction of manganese by CO-CO<sub>2</sub> was performed in an Applied Test Systems model 1379 rotating tube furnace. The furnace tube was made of Inconel 601 with a 5-in internal diameter. The furnace heating zone was 30 in long. Temperature control was provided by a Chromel-Alumel thermocouple connected to the furnace controller. Reduction temperature was maintained at a minimum ~625° C with the maximum of ~650° C. The ends of the tube were plugged with firebrick and sealed with Fiberfrax moldable refractory. The reduction gas was introduced into the furnace through a small hole in the center of the firebrick and consisted of a mixture of carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) in a ratio of 3:2 by weight and 2:33:1.0 by volume. Total flow rate was 1 L/min. The CO and CO<sub>2</sub> gases were of technical grade (98 pct) and chemically pure (CP) grade (99.8 pct), respectively. The reaction time was 4 h for 1,500 g of ground nodule feed. In a total of 11 reduction runs at these conditions, the average percent reduction of Mn<sup>4+</sup> to Mn<sup>2+</sup> was 96.2 ± 3.4 pct.

At the completion of 4 h, the ground reduced nodules were quenched in 1 L of distilled boiled water and were sparged with CO<sub>2</sub> gas for 3 h to facilitate carbonation of the manganese to manganese carbonate (MnCO<sub>3</sub>). After the CO<sub>2</sub> sparge, the reduced, carbonated nodules were divided into 150-g (dry basis) aliquots for use in the leaching step.



## Leaching-Aeration

The objective of the leaching-aeration operation is to oxidize and solubilize the value metals of Cu, Co, and Ni in an ammonia-ammonium carbonate solution while rejecting most of the Fe and Mn. The following are the principal chemical reactions occurring in this operation:



Reactions 9 through 13 are the solubilization of value metals including some iron (reaction 13). Reactions 13 through 15 show iron solubilization with the subsequent precipitation of iron as  $\text{Fe}(\text{OH})_3$  (reaction 15). In oxidizing conditions, the iron amine complex decomposes rapidly and forms insoluble ferric hydroxide  $\text{Fe}(\text{OH})_3$ , reaction 15 (18). Uncarbonated manganese may undergo either reaction 16 or 17. If  $\text{MnCO}_3$  is formed, the manganese is no longer available to be complexed and solubilized. Reaction 17 shows the formation of the hexamine manganese complex. This complex is also relatively unstable under oxidizing conditions and will decomplex.

The laboratory leaching-aeration operation was performed in glass 4-L stirred reaction vessels with compressed air sparged into the reaction vessel by fritted glass spargers located near the bottom. The leaching agent was a 100 g/L  $\text{NH}_3$  and 50 g/L  $\text{CO}_2$  solution prepared from  $\text{NH}_4\text{OH}$ ,  $(\text{NH}_4)_2\text{CO}_3$ , and  $\text{Na}_2\text{CO}_3$ . Total volume was 3 L and pulp density was 5 pct (150 g in 3 L). The reaction temperature was maintained at  $55^\circ \pm 5^\circ \text{C}$  for 1 h per stage in the four-stage countercurrent leach. Reaction vessels were covered to prevent excess  $\text{NH}_3$  vapor from escaping, and the operation was performed in a fume hood. The pH was maintained between 9.5 and 11.0 by addition of  $\text{NH}_4\text{OH}$  and  $\text{Na}_2\text{CO}_3$ . After equilibrium conditions were obtained in the four-stage countercurrent leach-aeration operation, 37 complete cycles were run and solids were collected for tailings washing. The operation consisted of leaching with the ammonia-ammonium carbonate solution with air sparged into the solution near the bottom of the vessel for 1 h, settling for 1 h, decanting the liquids to the next appropriate stage, and continuing the leaching as before. Because value metals are extracted during tailings washing as well as leaching, no leaching efficiencies are reported in this section. Typical composition of the completed fourth stage leach liquor, the depleted solids (tailings before washing), the dried nodule feed, and the reduced nodule feed are given in table 5. The depleted

**Table 5.—Gas reduction and ammoniacal leach process average compositions**

	Nodule feed, wt pct	Reduced nodule feed, wt pct	Pregnant leach liquor, g/L <sup>1</sup>	Unwashed tailings, wt pct
Mn	29.7 ± 0.6	41.0 ± 1.2	0.30 ± 0.19	33.7 ± 1.4
Fe...	5.46 ± .08	7.10 ± .47	<.001	6.39 ± .46
Cu...	1.20 ± .03	1.83 ± .11	.74 ± .10	.48 ± .17
Ni	1.33 ± .02	2.13 ± .38	.42 ± .08	1.00 ± .16
Co...	.23 ± .01	.39 ± .07	.042 ± .01	.22 ± .04
Zn...	.15 ± .01	.31 ± .09	.071 ± .04	.22 ± .20
Runs	NAP	11	34	37

NAP Not applicable. <sup>1</sup> 1 g/L = 1,000 µg/mL (ppm).

unwashed solids were collected and divided into six batches for tailings washing and solid-liquid separation.

## Tailings Washing and Solid-Liquid Separation

The objectives of the tailings washing and solid-liquid separation operation are to solubilize the remaining value metals and dewater the tailings to obtain a 30- to 50-pct solids content. Retention time per washing stage is on the order of 16 to 24 h for proposed commercial operations (4-5). The washed solids are steam stripped to recover ammonia.

Laboratory operation consisted of contacting the solids from leaching-aeration operations with wash liquid of 100 g/L  $\text{NH}_3$  and 50 g/L  $\text{CO}_2$  (prepared from  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{NH}_4\text{OH}$ , and  $\text{Na}_2\text{CO}_3$ ), at a slurry-to-liquid ratio of 2 kg of solids per kilogram of liquid. The tailings were agitated for 8 h and allowed to settle overnight. The settled solids were separated by decanting the liquid phase and were recontacted with fresh wash solution for a total of four complete stages. After separation of the fourth stage wash liquid, the solids were rinsed twice with distilled water at a 2-kg-solid-per-kilogram-liquid ratio to remove ammonia. This was done in lieu of steam stripping the relatively small amount of tailings. The final rinsed tailings were combined, blended, and placed into 1-gal plastic containers prior to analysis. Because of the primary interest in physical as well as chemical properties of the laboratory tailings, no flocculants were used to enhance settling characteristics.

The tailings were sampled from each 1-gal container and analyzed for elemental content, mineralogical composition, and leachability. A portion of the tailings was sent to the Bureau's Spokane (WA) Research Center where the physical property testing was performed.

## CUPRION AMMONIACAL LEACH PROCESS

The Cuprion ammoniacal leach process is analogous to the Caron (15) process used on nickeliferous laterites at Nicaro, Cuba (16), and Greenvale, Australia (17). Two major differences exist between the Caron process and that described for manganese nodules (4-5). The metals separation and purification is different for nodules, and the reduction step is different. The Cuprion process uses a near-ambient-temperature hydrometallurgical reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{2+}$  with excess  $\text{Cu}^+$  ion (19-20), whereas the Caron process uses the pyrometallurgical approach as outlined in the "Reduction and Quenching" section. A detailed flowsheet and process description is given in reference 4.

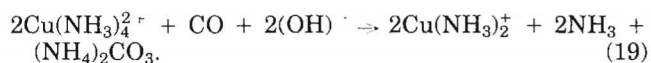
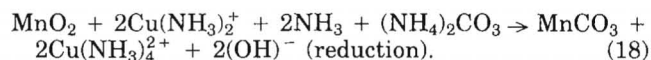
**Table 6.—Comparison of operating parameters and results for the Cuprion ammoniacal leach process**

Parameter and unit	Proposed commercial	Actual laboratory
<b>REDUCTION-LEACHING</b>		
Temperature .....°C..	50	55±5
Pressure..... atm.	1	1
Leachate composition, g/L:		
NH <sub>3</sub> .....	100	100
CO <sub>2</sub> .....	50	50
Cu .....	3-5	3.5
Number of stages .....	6	1
Mn reduction ..... pct.	97	96±4
Slurry density ..... pct solids.	20-30	20
<b>OXIDATION-LEACHING</b>		
Leachate composition, g/L:		
NH <sub>3</sub> .....	100	100
CO <sub>2</sub> .....	25	50
Temperature .....°C..	50	55
Pressure..... atm.	1	1
Solubilization, pct:		
Co .....	50	32
Cu .....	90	89.5
Fe.....	<1	<1
Mn .....	<1	<1
Ni .....	90	63
Time per stage .....h.	1	1
Number of stages .....	3	4
<b>SOLID-LIQUID SEPARATION</b>		
Slurry density..... wt pct.	35-40	31.1
Wash ratio ..... kg/kg liquid.	2	2
Wash liquid composition, g/L:		
NH <sub>3</sub> .....	100	100
CO <sub>2</sub> .....	50	50
Number of stages .....	6	6

A comparison between laboratory operating parameters and those suggested for the proposed commercial process (4-5) is given in table 6 for those unit operations performed in the laboratory. A complete list of proposed commercial parameters is available in reference 4.

### Reduction-Leaching

The objective of the Cuprion reduction-leaching operation is to disrupt the manganese nodule crystal structure (MnO<sub>2</sub>) by reducing the Mn<sup>4+</sup> to Mn<sup>2+</sup> and releasing the lattice-bound Co, Cu, and Ni for reduction and solubilization. By reducing Mn<sup>4+</sup> to Mn<sup>2+</sup>, the structure of the primary manganese minerals of todorokite, birnessite, and/or vernadite (3) are altered and the desired leaching agent is able to solubilize the value metals. In the Cuprion process, the reduction is performed by Cu<sup>+</sup> ion. The Cu<sup>+</sup> is regenerated with carbon monoxide. The primary reactions that occur in this portion of the process involving CO, Cu<sup>+</sup>, Mn, Fe, Cu, Ni, and Co are reactions 2 through 8 as previously given and the following reactions:



Reactions 18 and 19 show the reduction of Mn<sup>4+</sup> to Mn<sup>2+</sup> with the regeneration of the Cu<sup>+</sup> complex. Reactions 2 through 8 are the overall reduction-carbonation reactions producing MnCO<sub>3</sub>, and the reduction of iron and value metals of Cu, Ni, and Co to the elemental state. Once reduction is completed, the leach solution is aerated and oxidation leached as in the previous process.

The laboratory reduction-leaching operation was performed in 4-L stirred glass reactors with 1 L/min CO (technical grade of 98 pct) sparged into the vessel by fritted glass spargers located near the bottom. The initial cuprous ion was added as CuCl at a concentration of 3.5 g/L. The volume was 3 L of 100 g/L NH<sub>3</sub> and 50 g/L CO<sub>2</sub> solution prepared from reagent grade (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>OH, and Na<sub>2</sub>CO<sub>3</sub>. The reaction temperature was maintained at 55±5° C during the operation. After addition of CuCl, CO was sparged into the blue-colored solution until it became nearly colorless. Ground nodules were then added in 2-g increments and the pH and electromotive force (emf) were monitored. The pH was maintained between 10.0 and 11.0 by additions of NH<sub>4</sub>OH and Na<sub>2</sub>CO<sub>3</sub>; and the emf ranged from approximately -350 to -230 mV versus a calomel electrode with an average range of 90 mV per each 2-g increment of nodule addition. More nodule feed was added when the emf returned to near the initial reading. Nodules were added every few minutes until the emf cycle showed rapid return to the initial readings. This indicated that copper from the nodule feed was being solubilized, reduced to Cu(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>, and reacting with the manganese as shown in reactions 18 and 19. At this point, the nodule feed increments were increased gradually to 5, 10, and finally 25 g. The reaction was terminated when the pulp density reached ~20 pct or when 600 g of nodules had been added, and a new reduction-leaching operation started. The reduced carbonated nodules from the reactor were sampled and analyzed for manganese as Mn<sup>2+</sup>. In a total of 21 runs, the average percent manganese reduction was 95.8±4.1. These reduced nodules were used as feed to a four-stage countercurrent oxidation leach to solubilize the remaining value metals.

### Oxidation-Leaching

The objective of the oxidation-leaching operation is to oxidize and solubilize the value metals of Cu, Co, and Ni in ammonia-ammonium carbonate solution while rejecting most of the Fe and Mn. The chemical reactions occurring in this operation are reactions 9 through 12 and 14 through 17.

Reactions 9 through 12 are the solubilization of value metals including some iron (reaction 12). Reactions 14 and 15 show the solubilization of iron and its subsequent precipitation as Fe(OH)<sub>3</sub> (reaction 15). In oxidizing conditions, the iron amine complex decomposes rapidly forming insoluble ferric hydroxide [Fe(OH)<sub>3</sub>] (18). Uncarbonated manganese may undergo either reaction 16 or 17. If MnCO<sub>3</sub> is formed, the manganese is no longer available to be complexed and solubilized. Reaction 17 is the formation of the hexamine manganese complex, which is also relatively unstable under oxidizing conditions and will decompose.

The laboratory oxidation-leaching operation was performed in the same manner as the similar operation for the previous process and its description is not repeated here. Because value metals are solubilized in the reduction leach, oxidation leach, and the tailings washing, no leaching efficiencies are reported. Typical composition of the completed fourth stage leach liquor, the depleted solids, and the dried nodule feed are given in table 7. The depleted unwashed solids were collected and divided into nine batches for tailings washing and solid-liquid separation.

Table 7.—Cuprion process average compositions

	Nodule feed, wt pct	Pregnant leach liquor, g/L <sup>1</sup>	Unwashed tailings, wt pct
Mn...	29.7 ± 0.6	0.05 ± 0.2	25.5 ± 3.4
Fe...	5.46 ± .08	<.001	4.97 ± .61
Cu...	1.20 ± .03	1.14 ± .23	.55 ± .32
Ni...	1.33 ± .02	.24 ± .03	.79 ± .20
Co...	.23 ± .01	.026 ± .007	.18 ± .01
Zn...	15 ± .01	.018 ± .010	.09 ± .06
Runs	NAP	45	45

NAP Not applicable. <sup>1</sup> 1 g/L = 1,000 µg/mL (ppm).

### Tailings Washing and Solid-Liquid Separation

The objective of the tailings washing and solid-liquid separation operation is to solubilize the remaining value metals and dewater the tailings to obtain a 30- to 50-pct solids content. Retention time per washing stage is on the order of 16 to 24 h for proposed commercial operation (4-5). The washed solids are steam stripped to recover ammonia. The rinsed tailings were combined, blended, and placed into 1-gal plastic containers prior to analysis. Because of the interest in physical as well as chemical properties of the laboratory tailings, no flocculants were used to enhance settling characteristics. The tailings were sampled from each container and analyzed for elemental content, mineralogical composition, and leachability. A portion of the tailings was sent to the Bureau's Spokane (WA) Research Center where the physical property testing was performed.

The Cuprion process is the only process for which the industry supplied pilot-plant generated tailings. These tailings were also tested, and results of the laboratory and pilot-plant generated tailings are compared in the "Tailings Characterization" section.

### HIGH-TEMPERATURE AND HIGH-PRESSURE SULFURIC ACID LEACH PROCESS

The high-temperature and high-pressure sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) leach process is analogous to the process used at Moa Bay, Cuba, on nickeliferous laterites (21-22). The major differences between the proposed nodule process and the Moa Bay, Cuba, operation are the metals separation and purification steps which are complicated in the proposed process by the chemical similarity of copper, nickel, and cobalt. Process flowsheets and detailed descriptions are given elsewhere (4).

A comparison between laboratory operating parameters and those suggested for the proposed commercial process (4-5) is given in table 8 for those unit operations performed in the laboratory. A complete list of proposed commercial parameters is available in reference 4.

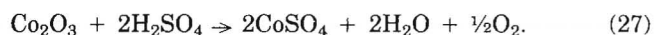
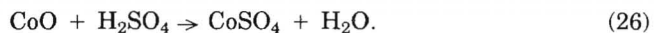
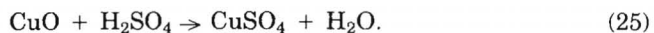
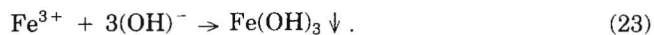
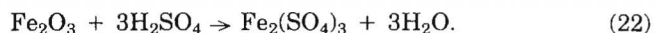
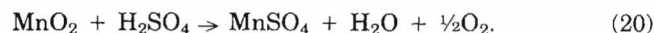
#### Leaching

The objective of the leaching operation is to disrupt the manganese nodule crystal structure (MnO<sub>2</sub>) by initially reducing Mn<sup>4+</sup> to Mn<sup>2+</sup> allowing the lattice-bound Co, Cu, and Ni to be solubilized. In this process, the reduction of Mn<sup>4+</sup> to Mn<sup>2+</sup> and the solubilization of Co, Cu, and Ni occur in the same reactor. As the acid is depleted, Mn<sup>2+</sup> is reoxidized to Mn<sup>4+</sup> and remains in the tailings as MnO<sub>2</sub>. This acid depletion also permits iron to

Table 8.—Comparison of operating parameters and results for the high-temperature and high-pressure sulfuric acid leach process

Parameter and unit	Proposed commercial	Actual laboratory
LEACHING		
Temperature.....°C.	245	245 ± 3
Pressure.....psig.	515	530 ± 5
Contact time.....h.	4	1.5
H <sub>2</sub> SO <sub>4</sub> consumption...lb/lb nodules.	0.4	0.4
Solubilization, pct:		
Co.....	90	92
Cu.....	95	95
Fe.....	1	12
Mn.....	5	5
Ni.....	95	98
SOLID-LIQUID SEPARATION		
Number of stages.....	6	8
Slurry density.....pct solids.	35-40	30.5
Wash ratio.....kg/kg liquor.	2	2

precipitate as the hydroxide Fe(OH)<sub>3</sub>. The following are the primary chemical reactions that occur during the leaching operation for the major and minor metals of interest:



Reactions 20 and 21 are the disruption of the manganese MnO<sub>2</sub> structure and the subsequent reoxidation at low acid strengths to MnO<sub>2</sub>. Reactions 22 and 23 show the solubilization of iron and its subsequent reprecipitation at low acid strengths. Another possible iron product is jarosite, KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>, but no reaction is given because it should only be a minor product reacting with the available potassium. If seawater is used for all or part of the liquid; then jarosite would form in larger quantities. Reactions 24 through 27 show the solubilization of the value metals Co, Cu, and Ni. Molybdenum probably is not solubilized in the process and remains with the tailings. If molybdenum is solubilized during leaching, it is subsequently precipitated at the low acid strengths, possibly with the iron hydroxides.

The laboratory leaching operation was performed in a Parr Instruments model 4522, 2-L stirred pressure reactor. The reactor bomb was made of titanium and had a glass liner. Temperature control was provided by a Chromel-Alumel thermocouple connected to the controller. Temperature was maintained at 245° ± 3° C. Each run was made with 400 g of minus 80-mesh nodules and 111 mL of H<sub>2</sub>SO<sub>4</sub> combined with 750 mL of H<sub>2</sub>O. This gave a reagent-to-nodule ratio of 0.4 lb H<sub>2</sub>SO<sub>4</sub>/lb nodule. Pressure inside the bomb was maintained at 530 ± 5 psig. The nodules and acid-H<sub>2</sub>O mixture were combined just prior to startup, and the bomb sealed and brought to temperature in 60 min. Reaction time at 245° ± 3° C and 530 ± 5 psig was



Table 9. — High-temperature and high-pressure sulfuric acid leach process average compositions

	Nodule feed, wt pct	Pregnant leach liquor, g/L <sup>1</sup>	Unwashed tail- ings, wt pct
Mn...	29.7 ± 0.6	6.48 ± 0.40	32.0 ± 2.30
Fe...	5.46 ± .08	2.82 ± .42	5.94 ± .47
Cu...	1.20 ± .03	4.76 ± .29	.12 ± .03
Ni...	1.33 ± .02	5.48 ± .40	.030 ± .022
Co...	.23 ± .01	.91 ± .06	.035 ± .010
Zn...	.15 ± .01	.56 ± .05	.042 ± .016
Runs	NAP	55	55

NAP Not applicable. <sup>1</sup>1 g/L = 1,000 µg/mL (ppm).

90 min, and cooling required an additional 60 min. Generally two runs were made each day and a total of 55 runs were made to collect tailings. After completion of the cooldown period, the nodule residue and pregnant liquor were separated by filtration, and samples of the liquid and solid portions were analyzed for Mn, Fe, Cu, Ni, Co, and Zn. Typical average composition of the pregnant liquor, unwashed tailings, and nodule feed composition for the 55 runs are given in table 9. After completion of the runs, the unwashed tailings were combined into eight batches and subjected to solid-liquid separation and tailings washing.

### Solid-Liquid Separation

The objective of the solid-liquid separation operation is to remove entrained leach liquor and recover the remaining value metals. Final tailings slurry density should be between 30 to 50 pct solids content.

The laboratory operation consisted of contacting the solids from the leaching operations with 2.0-pH wash liquid made with H<sub>2</sub>SO<sub>4</sub> at a tailings slurry-to-liquid ratio of 2 kg solids/kg liquid. The tailings were agitated for 6 h and allowed to settle. The liquid portion was decanted and the solids were contacted with fresh wash solution for a total of eight complete stages. After separation of the eighth stage wash liquid, the solids were combined, blended, and placed into 1-gal plastic containers prior to analysis. Because of the interest in physical as well as chemical characteristics of the laboratory tailings, no flocculants were used to enhance settling characteristics.

Samples from each container were analyzed for elemental content, mineralogical composition, and leachability. A portion of the tailings was sent to the Bureau's Spokane (WA) Research Center where the physical property testing was performed.

## REDUCTION AND HYDROCHLORIC ACID LEACH PROCESS

The reduction and hydrochloric acid leach process has no direct analog in existing ore processing. Detailed flowsheets and process descriptions are given elsewhere (4).

A comparison between laboratory operating parameters and those suggested for the proposed commercial process (4-5) is given in table 10 for those unit operations performed in the laboratory. A complete list of proposed commercial parameters is available in reference 4.

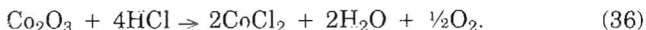
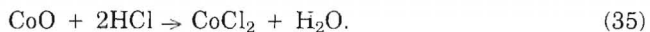
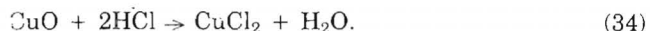
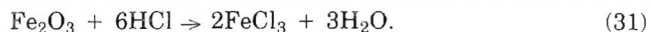
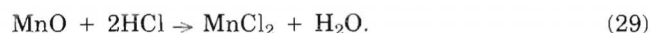
### Hydrochlorination

The principle of the hydrochlorination operation is to reduce and chlorinate manganese and to chlorinate the

Table 10. — Comparison of operating parameters and results for the reduction and hydrochloric acid leach process

Parameter	Proposed commercial	Actual laboratory
HYDROCHLORINATION		
Temperature .....	500	500
Pressure .....	1	1
Reagent .....	HCl gas	HCl gas
Percent excess HCl .....	100	100
Hydrolysis temperature .....	200	100
Hydrochlorination, pct:		
Co .....	100	94
Cu .....	96	94
Fe .....	27	20
Mn .....	94	97
Ni .....	100	98
LEACHING AND WASHING		
Final pH .....	2.0	2.3
Slurry density .....	20-25	32
Wash ratio .....	2:1	2:1
Number of stages .....	6	6
Soluble metals removed .....	98	98

value metals of cobalt, copper, and nickel. In this step, Mn<sup>4+</sup> is reduced to Mn<sup>2+</sup> and chlorine is released. This reduction allows subsequent release of the value metals and their chlorination. As the reaction is completed, water is sprayed into the furnace to hydrolyze iron to Fe<sup>3+</sup> hydroxide and the iron is precipitated as Fe(OH)<sub>3</sub>. The principal chemical reactions that occur during hydrochlorination are as follows for the major and minor metals of interest:



Reactions 28 and 29 are the stepwise reduction and hydrochlorination of MnO<sub>2</sub> with reaction 30 being the overall net reaction. Reaction 31 is the chlorination of iron to form FeCl<sub>3</sub>. As shown, this reaction forms water that can react with iron during hydrolysis to form Fe(OH)<sub>3</sub> (reaction 32). Reactions 33 through 36 show the chlorination of the value metals Co, Cu, and Ni. Many other components of nodules are solubilized including Mo, V, Zn, and alkali and alkaline earth elements. Elements such as Al, Pb, Ti, and Tl are also solubilized by the high-chloride media.

The laboratory hydrochlorination operation was performed in an Applied Test System model 1379 rotating tube furnace with a 5-in-ID Inconel 601 tube. The temperature in the 30-in heating zone was controlled by a Chromel-Alumel thermocouple connected to the furnace controller. The temperature was maintained at 510° ± 10° C for the 8 h of each run. Technical grade HCl gas (99.0 pct) was added at a rate of 1.5 L/min to provide the 100 pct excess HCl for the 625 g of nodule feed. At the end of the 8 h, the gas was shut off and the furnace allowed to bake off the excess HCl. The furnace was raised to allow the

chlorinated nodules to tumble into 1.5 L of boiling distilled water for hydrolysis and quenching.

Because of the corrosivity of HCl gas at temperatures over 450° C, corrosion of the Inconel 601 tube took place during each run which added chromium and additional nickel and iron to the solid phase. The amount of nickel and chromium added was calculated based on the chromium content as nodules contain very little chromium (<50 µg/g). The value of nickel associated with chromium in Inconel 601 was taken into account when determining nickel efficiencies.

A total of 61 hydrochlorination runs was performed. The chlorinated nodules were collected and treated with aqueous HCl to complete the dissolution and solubilization of the value metals.

### Leaching and Tailings Washing

The leaching and tailings washing operation is designed to solubilize the value metals of Co, Cu, Mn, and Ni, reject most of the iron to the tailings, and wash the tailings prior to disposal. Final solids content should be 30 to 50 pct by weight.

The laboratory operation consisted of leaching the chlorinated nodules with aqueous HCl at mild temperatures of approximately 80° C to complete dissolution of the value metals. The final pH of the leach solution was between 2.0 and 2.3. The solution pH was adjusted to 3.2 to precipitate the remaining iron and the solids and liquids were separated. The tailings were washed six times to simulate the proposed commercial operation and were filtered. The final pH was 6.5 and final solids content was 32 wt pct. The 26.3 lb of tailings (dry weight) was blended and divided among six 1-gal plastic containers prior to analysis. Table 11 gives the quench liquor, unwashed tailing solids, and nodule feed composition for Mn, Fe, Co, Cu, Ni, and Zn. Because of the interest in physical properties of the tailings as well as chemical characteristics, no flocculants were used to enhance settling properties.

Samples from each container were analyzed for elemental content, mineralogical composition, and leachability. A portion of the tailings was sent to the Bureau's Spokane (WA) Research Center where the physical property testing was performed.

### SMELTING AND SULFURIC ACID LEACH PROCESS

Copper, nickel, cobalt, and a ferromanganese alloy, if desired, can be recovered from nodules by a smelting and

**Table 11. — Reduction and hydrochloric acid leach process average compositions**

	Nodule feed, wt pct	Quench liquid, g/L <sup>1</sup>	Unwashed tail- ings, wt pct
Mn....	29.7 ± 0.6	40.4 ± 1.2	10.57 ± 1.91
Fe....	5.46 ± .08	.20 ± .07	13.50 ± 1.44
Cu....	1.20 ± .03	1.40 ± .50	.36 ± .09
Ni....	1.33 ± .02	3.16 ± .98	<sup>2</sup> 2.24 ± .76
Co....	.23 ± .01	.33 ± .14	.10 ± .03
Zn....	.15 ± .01	.23 ± .07	.04 ± .03
Runs	NAP	61	61

NAP Not applicable.

<sup>1</sup> 1 g/L = 1,000 µg/mL (ppm).

<sup>2</sup> Contaminated by Inconel 601 tube.

**Table 12. — Comparison of operating parameters and results for the smelting and sulfuric acid leach process**

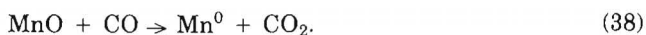
Parameter and unit	Proposed commercial	Actual laboratory
<b>REDUCTION-SMELTING</b>		
Reductants.....	Coke CO	Coke CO
Temperature, °C:		
Reduction.....	725	725
Smelting.....	1,325	1,400
Reduction time.....h.	2	1.5
Flux.....	Silica	Silica
Alloy recovery, pct:		
Co.....	90	97
Cu.....	90	98
Fe.....	70	94
Mn.....	2	2
Ni.....	95	99
Slag recovery, pct:		
Co.....	<10	3
Cu.....	<10	2
Fe.....	20	6
Mn.....	98	98
Ni.....	<10	1
<b>FERROMANGANESE REDUCTION</b>		
Reductant.....	Coke	Coke
Flux.....	Lime	Lime
Alloy composition, pct:		
Mn.....	78	75
Fe.....	14	6
C.....	7	7.6
SiO <sub>2</sub> .....	1	3.8

sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) leach process. Detailed flowsheets and process descriptions are given elsewhere (4).

A comparison between laboratory operating parameters and those suggested for the proposed commercial process (4-5) is given in table 12 for those unit operations performed in the laboratory. A complete list of proposed commercial parameters is available in reference 4.

### Reduction-Smelting

The objective of the reduction-smelting operation is to disrupt the manganese minerals by reducing Mn<sup>4+</sup> to Mn<sup>2+</sup> and releasing lattice-bound Co, Cu, and Ni for reduction. The elements Co, Cu, and Ni are reduced to the metallic state, Co<sup>0</sup>, Cu<sup>0</sup>, Ni<sup>0</sup>, as is most of the iron present. Under controlled conditions, the manganese is not reduced to Mn<sup>0</sup> but remains as Mn<sup>2+</sup> in the slag. The Co, Cu, Fe, and Ni form a metal alloy that settles by density difference to the bottom of the reaction vessel. The reduction is performed by using coke and CO-rich gas and silica is used as the flux for slagging. The primary reactions that occur in this portion of the process involving C, CO, SiO<sub>2</sub>, Mn, Fe, Cu, Ni, and Co are reactions 2, 5, 6, 8, and the following:





Reactions 2, 37, and 38 show the various steps for the reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{2+}$  and to  $\text{Mn}^0$ . Reactions 39 and 40 are slag formations and reaction 41 shows the reoxidation of  $\text{Mn}^0$  to  $\text{Mn}^{2+}$  by controlled blowing operations. Reactions 5, 6, 8, and 42 through 47 show the various steps and mechanisms for Fe, Cu, Ni, and Co reduction to the metallic state. Once the reduction is complete, the metal alloy separates from the oxide-silicate slag by gravity.

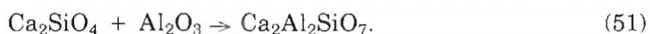
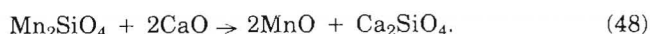
The laboratory reduction-smelting operation was performed as a single operation in a Lindberg electric resistance furnace type 56953 with temperature control from  $500^\circ$  to  $1,500 \pm 1^\circ \text{C}$ . A type R (Pt versus Pt-13 pct Rh) thermocouple was connected to a phase angle fired temperature controller (Lindberg type 59645). A mixture of 1,900 g of nodules, 100 g of coke, and 350 g of silica was blended for 2 h and placed in a size 16 SiC graphite-bonded crucible. The crucible was then placed in a  $160^\circ \text{C}$  drying oven overnight. The coke added had the amount of carbon equivalent required to reduce all the  $\text{Mn}^{4+}$  to  $\text{Mn}^{2+}$ , and all the Fe, Cu, Co, and Ni to the metallic state. The silica was added to complex the  $\text{Mn}^{2+}$  as  $\text{MnSiO}_3$  or  $\text{Mn}_2\text{SiO}_4$  to keep the manganese in the slag phase. After drying overnight, the crucible was placed in the high-temperature furnace ( $500^\circ \text{C}$ ) and a refractory brick lid placed on top. The furnace was closed and the controller set for  $1,400^\circ \text{C}$ . Heat-up time to  $1,400^\circ \text{C}$  was approximately 6 h and allowed the initial reduction step to occur. The temperature was maintained at  $1,400^\circ \pm 1^\circ \text{C}$  for 1.5 h and the furnace controller was then reset to  $500^\circ \text{C}$  (minimum temperature). The charge was removed after overnight cooling and then a new, previously dried crucible with nodule-coke-silica was inserted in the furnace. After cooling to near room temperature, the slag and metal were removed with an impact drill. A total of 35 runs were made with an average metal weight of  $173 \pm 9 \text{ g}$  and slag weight of  $1,600 \pm 84 \text{ g}$ . A total of 56 kg of slag and 6 kg of metal were produced. Table 13 gives the average compositions of the nodule feed material, slag, and metal for the 35 runs. Approximately 98 pct of the manganese reported in the slag phase and 94 pct of the iron reported to the alloy. Value metal recoveries were all greater than

97 pct. The slag generated was ground to minus 100 mesh, blended, and divided into five batches for analysis.

To prove process feasibility, several metal buttons were remelted, combined with silica, and blown with air to remove the remaining Mn and some Fe. The commercial operation requires low Mn levels in the metal alloy so that sulfur consumption during sulfidizing and matte formation is kept to a low level. The several tests run in the laboratory yielded Mn levels less than the maximum of 0.1 pct. The slag produced in this step would be recycled back to the smelting step to recover any value metals loss during the blowing operation.

## Ferromanganese Reduction

The objective of the ferromanganese reduction operation is to convert the slags generated in the smelting furnace to ferromanganese and a calcium and aluminum silicate slag. The slags from the smelting operation are fluxed with CaO (lime) and possibly additional silica, and coke is added as a reductant. This allows the Ca to react with the silicates in the slag along with Al and other slag-forming elements to form  $\text{Ca}_2\text{SiO}_4$ ,  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ , and other silicates. The coke reacts with the Mn and Fe to form the metals in a ferromanganese alloy that separates by gravity from the slags. The primary reactions that take place in this operation are reaction 39 and the following:



Reactions 39, and 48 through 50 show the reactions of lime with the manganese silicates and the subsequent reduction of  $\text{Mn}^{2+}$  to  $\text{Mn}^0$ . Reactions 48, 51, and 52 show formation of gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) and larnite ( $\beta\text{-Ca}_2\text{SiO}_4$ ).

The laboratory generation consisted of mixing 1,000 g of slag from the reduction-smelting operation with 100 g coke and 840 g lime. The coke is the amount required to reduce the MnO to  $\text{Mn}^0$  and the lime is twice the amount needed to convert  $\text{Mn}_2\text{SiO}_4$  to  $\text{Ca}_2\text{SiO}_4$ . The sample mixture was placed in a size 16 SiC crucible and the crucible placed in the Lindberg furnace. The temperature controller was set for  $1,450^\circ \text{C}$  and required 7 h to reach temperature. The mix was held at  $1,450^\circ \text{C}$  for 1 h and allowed to cool to  $500^\circ \text{C}$  overnight. The next morning the crucible was removed, cooled to near room temperature, and the product removed. After two successful runs, the furnace failed to heat properly. The smelting slag had proven nonhazardous so that the slag produced in the ferromanganese runs was likely to be the same. The slag and metal alloy were used for analyses. The slags contained  $\beta\text{-Ca}_2\text{SiO}_4$  (larnite),  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  (gehlenite), and excess  $\text{SiO}_2$  (silica) as the primary minerals. The metal was very friable and contained 75 pct Mn and about 6 pct Fe. Table 13 gives the slag analysis and metal analysis for the ferromanganese operation.

**Table 13. — Smelting and sulfuric acid leach process average compositions, weight percent**

	Nodule feed	Metal alloy	Smelting slag	Ferromanganese	
				Alloy	Slag
Mn....	29.7 ± 0.6	9.2 ± 2.0	29.7 ± 2.8	75.1	5.35
Fe....	5.46 ± .08	48.6 ± 7.0	.30 ± .18	6.1	.07
Cu....	1.20 ± .03	12.4 ± 2.5	.03 ± .02	.24	.07
Ni....	1.33 ± .02	14.6 ± 2.3	.02 ± .02	.17	<.01
Co....	.23 ± .01	2.54 ± .36	.009 ± .002	.03	<.001
Zn....	.15 ± .01	.05 ± .04	.014 ± .009	.03	.004
SiO <sub>2</sub>	13.4	1.65 ± .56	41.7 ± .1	3.8	33.9
C.....	12	2.76 ± .33	.51 ± .01	7.6	1.74
Runs.	NAP	35	35	2	2

NAP Not applicable.

## TAILINGS CHARACTERIZATION

After completion of the laboratory processing, the blended tailings were characterized by a variety of tests and analyses. The results of these tests and analysis are reported in the following order: physical property testing, mineralogical analyses, chemical analyses, and leachate testing. The primary elements of interest are those elements on the Toxic Substance Control Act list of priority pollutants, the Resource Conservation and Recovery Act list of leachable metals for EP toxicity, and/or major and minor elements of economic importance. The elements are Ag, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, and Zn. Mercury was not determined because of its extremely low level in nodules (2-3).

Results reported are for all process tailings generated, and the following acronyms are used for the processes presented in the data tables and text.

Gas reduction and ammoniacal leach — GRaML  
Cuprion ammoniacal leach-laboratory — CuAmL-Lb  
Cuprion ammoniacal leach-pilot plant — CuAmL-Pp  
High-temperature and high-pressure sulfuric acid leach — HTPSAL

Reduction and hydrochloric acid leach RHCIAL  
Smelting and sulfuric acid leach — SmSAL (SmSAL-1 and SmSAL-2)

The acronym SmSAL-1 is used to denote the smelting slag and SmSAL-2 is used to denote the ferromanganese slag. The analyses and testing of the tailings were done immediately after the laboratory operations were completed so that tailings did not age significantly before characterization.

### PHYSICAL PROPERTY TESTING RESULTS

The tests performed on the tailings for physical properties are listed in table 1. In the case of the GRaML process, triaxial shear, permeability, and maximum density were not tested because of insufficient sample volume for these tests. The slags from the SmSAL process were not tested for physical properties as they were glassy and massive. The particle size is dependent on the amount of granulation or crushing that takes place for slags and many other parameters do not apply and/or are dependent on the particle size distribution.

The results shown in table 14 from the GRaML,

**Table 14. — Physical properties of tailings from laboratory and pilot-plant leach processes<sup>1</sup>**

Parameter	GRaML	CuAmL-Lb	CuAmL-Pp	HTPSAL	RHCIAL
Grain size distribution, $\mu\text{m}$ :					
100 pct pass .....	600	600	74	600	425
50 pct pass .....	29	13	6	15	14
0 pct pass .....	0.6	1	1	1	1.2
Specific gravity, dry solids	3.47	3.10	3.19	3.49	2.85
Triaxial shear <sup>2</sup> .....	ND	38.5°	38.0°	5.2°	38.5°
Friction angle .....	ND	4.0	5.0	8.6	0.0
Cohesion .....	psi..				
Permeability <sup>2</sup> 10 <sup>-5</sup> cm/s ..	ND	0.67	0.85	70	1.23
Maximum density .. pct ..	ND	92.5	90.1	87.7	57.0
Atterberg limits:					
Liquid .....	pct..	43.8	42.1	45.0	43.3
Plastic .....	pct..	39.4	34.4	41.2	43.7
Soil class .....	ML	ML	ML	ML	MH
Percent solids .... wt pct ..	29.4	31.1	41.8	30.5	32.0

MH Diatomaceous silt. ML Lean silt. ND Not determined.

<sup>1</sup> Analyses performed at the Bureau's Spokane Research Center, Spokane, WA, and coordinated by R. W. McKibben, mining engineer.

<sup>2</sup> At 98 pct of maximum density.

CuAmL-Lb, and CuAmL-Pp are very similar to each other as predicted (2). The tailings from the HTPSAL process are similar to the three ammoniacal leach processes. The RHCIAL process tailings are substantially different from those derived from the three ammonia-based and HTPSAL processes with a lower specific gravity and maximum density but the RHCIAL does have a similar particle size distribution. The lower specific gravity for the RHCIAL process tailings is because of the absence of manganese, making the composition primarily iron oxides and hydroxides, silica, and feldspar.

### MINERALOGICAL ANALYSES RESULTS

Air-dried samples of the tailings and slags were examined by X-ray diffraction (XRD) to determine the major and minor minerals present. With the exception of the SmSAL-1 and SmSAL-2 slags, from the SmSAL process, a second set of tailings samples was acid leached with aqueous HCl and the washed air-dried residue was also examined using XRD.

The results of the XRD analysis are given in table 15.

**Table 15.—Mineralogical analyses of tailings and slags from laboratory and pilot-plant leach processes<sup>1</sup>**

Mineral	Chemical formula	Concentration, <sup>2</sup> qualitative values						
		GRaML	CuAmL-Lb	CuAmL-Pp	HTPSAL	RHCIAL	SmSAL-1	SmSAL-2
Feldspars .....	NaAlSi <sub>3</sub> O <sub>8</sub> , KAlSi <sub>3</sub> O <sub>8</sub> , CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	Low .....	Low .....	Low .....	Very low ..	Minor .....	ND .....	ND .....
Gehlenite .....	Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>	ND .....	ND .....	ND .....	ND .....	ND .....	ND .....	Major ..
Hausmannite .....	Mn <sub>2</sub> O <sub>4</sub>	Minor .....	ND .....	ND .....	Minor .....	ND .....	ND .....	ND .....
Hematite .....	Fe <sub>2</sub> O <sub>3</sub>	ND .....	ND .....	ND .....	ND .....	Low .....	ND .....	ND .....
Iron oxides and hydroxides.	FeO, Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub> , Fe(OH) <sub>3</sub>	ND .....	ND .....	ND .....	Minor .....	Low .....	ND .....	ND .....
Larnite .....	$\beta$ -Ca <sub>2</sub> SiO <sub>4</sub>	ND .....	ND .....	ND .....	ND .....	ND .....	ND .....	Major ..
Pyrolusite .....	MnO <sub>2</sub>	ND .....	ND .....	ND .....	Minor .....	ND .....	ND .....	ND .....
Quartz .....	SiO <sub>2</sub>	Very low ..	Very low ..	Very low ..	Very low ..	Low .....	ND .....	ND .....
Rhodochrosite .....	MnCO <sub>3</sub>	Major .....	Major .....	Major .....	ND .....	ND .....	ND .....	ND .....
Rhodonite .....	MnSiO <sub>3</sub>	ND .....	ND .....	ND .....	ND .....	ND .....	Low .....	Very low.
Tephroite .....	Mn <sub>2</sub> SiO <sub>4</sub>	ND .....	ND .....	ND .....	ND .....	ND .....	Major .....	ND .....

ND Not detected.

<sup>1</sup> Analysis performed by C. W. Huggins, research chemist, Avondale Research Center, Avondale, MD.

<sup>2</sup> Major, >25 wt pct; minor, 10-25 wt pct; low, 5-10 wt pct; very low, <5 wt pct.



The primary constituents of the three ammoniacal processes — GRAmL, CuAmL-Lb, and CuAmL-Pp — were rhodochrosite ( $\text{MnCO}_3$ ) and hausmannite ( $\text{Mn}_3\text{O}_4$ ) with minor amounts of quartz and feldspar. The  $\text{Mn}_3\text{O}_4$  was primarily observed in the GRAmL process tailings because of incomplete carbonation. The acid insoluble fraction of all process tailings contained quartz and feldspar. The HTPSAL tailings contained poorly crystalline  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}_2$ , and iron oxide compounds with low amounts of quartz and feldspar. The RHCIAL tailings contained  $\text{Fe}_2\text{O}_3$ , quartz, and feldspar. The slags from the SmSAL process were  $\text{Mn}_2\text{SiO}_4$  and  $\text{MnSiO}_3$  for the slag produced from smelting the nodules and  $\text{Ca}_2\text{SiO}_4$  and  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  for the ferromanganese reduction slags.

## CHEMICAL ANALYSES RESULTS

The blended tailings from the tailings washing solid-liquid separation operations were sampled. The solid and liquid phases were analyzed from the GRAmL, CuAmL-Lb, CuAmL-Pp, HTPSAL, and RHCIAL processes and the solid phase slags from the SmSAL process as it produces no liquids. The liquid phase samples were analyzed directly by atomic absorption spectrophotometry (AAS) and ion chromatography (IC) for elemental and ion content, respectively. Although the liquid concentration levels will vary depending on washing completeness and percent solids, results are given here to bring attention to the probable low levels that will be attained. The solid phase samples were dried, dissolved by procedures outlined previously (1, 14), and the solutions analyzed by AAS and IC. A total of 25 elements and 7 anions were determined in each phase. In addition, pH,  $\text{CO}_2$  as carbonate, and ammonium ion ( $\text{NH}_4^+$ ) were determined in

the liquid phase; and divalent manganese ( $\text{Mn}^{2+}$ ) and  $\text{NH}_4^+$  were determined in the solid phase. Solid phase  $\text{CO}_3^{2-}$  was determined by Leco carbon analyzer, and liquid phase  $\text{CO}_3^{2-}$  was determined by IC. The elements As, Sb, and Se were determined by electrothermal atomization AAS. Mercury was not determined because of extremely low levels in nodules (2-3). Tables 16 and 17 contain results of solid phase analyses with table 16 containing elemental values. Table 17 contains analyses results for the ions  $\text{NH}_4^+$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  for solid and liquid phase samples. Table 18 contains the elemental analyses results of the liquid phase samples.

Eight additional elements were analyzed for semi-quantitatively by optical emission spectroscopy. These elements, concentration ranges, and detection limits are given in table 19.

## LEACHATE TESTING RESULTS

The tailings and slags from the laboratory and pilot plant leach processes were evaluated using three independent leachate tests, each run in duplicate. The three tests are the EPA extraction procedure (EP) toxicity test (9), the ASTM shake extraction test (10), and the EPA-COE seawater elutriant test (11). These tests are described in each of the following sections, along with the results obtained.

### EP Toxicity Test

According to EPA regulations under the Resource Conservation and Recovery Act (23), a solid waste must be listed as a hazardous waste if it exhibits any of the following characteristics: ignitability, corrosivity, reactiv-

Table 16.—Elemental analytical results for tailings solids and slags from laboratory and pilot-plant leach processes

Element	Analysis working limits <sup>1</sup>	Process and number of replicates						
		GRAML (5)	CuAmL-Lb (6)	CuAmL-Pp (5)	HTPSAL (6)	RHCIAL (6)	SmSAL-1 (5)	SmSAL-2 (4)
WEIGHT PERCENT								
Al.....	0.0075	2.53	2.28	2.37	2.0	4.3	2.8	3.16
Ba.....	.004	.20	.16	.24	.35	.47	.10	.15
Ca.....	.00025	1.58	1.42	1.60	1.5	.40	.46	24.8
Co.....	.001	.24	.22	.18	.04	.037	.005	<.001
Cu.....	.00025	.29	.31	.14	.12	.19	.06	.016
Fe.....	.0005	5.88	5.67	5.80	8.63	9.6	.95	.32
K.....	.0002	.38	.23	.59	.98	.25	.06	.06
Mg.....	.00002	2.20	2.11	2.03	.05	.29	1.64	2.07
Mn.....	.00025	33.7	27.0	27.0	32.8	1.93	31.5	6.40
Mn <sup>2+</sup> .....	.00025	26.4	20.5	27.0	1.13	.54	25.4	5.3
Mo.....	.002	<.002	<.002	.0068	.13	.079	<.002	<.002
Na.....	.00003	1.57	1.10	.98	.095	.87	1.95	.23
Ni.....	.001	.86	.56	.22	.048	<sup>2</sup> 1.15	.02	<.001
Pb.....	.001	.045	.042	.041	.033	.017	<.001	<.001
Si (SiO <sub>2</sub> ).....	.5	13.5	13.1	12.6	16.8	58.5	41.7	33.9
Ti.....	.02	.53	.42	.32	.71	1.43	.54	.24
V.....	.01	.10	.09	.07	.10	.11	.04	<.01
Zn.....	.00005	.13	.11	.13	.018	.007	.003	.034
MICROGRAMS PER GRAM								
Ag.....	1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
As.....	.5	58	52	49	60	208	<.5	.7
Be.....	1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
Cd.....	.5	14	20	20	4	<.5	.9	<.5
Cr.....	10	<10	<10	<10	30	<sup>2</sup> 16,000	400	150
Li.....	1.5	72	68	115	<1.5	<1.5	30	51
Sb.....	.6	68	49	40	40	123	<.6	<.6
Se.....	.6	<.5	2.0	1.2	2.0	1.0	.7	<.5
Tl.....	30	78	73	83	95	<30	<30	<30

<sup>1</sup> Results below these limits are reported as less than (<) the limits. Limits are based on 2 g in 100 mL.

<sup>2</sup> Contaminated by Inconel 601 tube.

**Table 17. — Ion analyses results for tailings solids, slags, and liquids from laboratory and pilot-plant leach processes**

Ion	Analysis working limits <sup>1</sup>	Process and number of replicates						
		GRAML (5)	CuAmL-Lb (6)	CuAmL-Pp (5)	HTPSAL (6)	RHCIAL (6)	SmSAL-1 (5)	SmSAL-2 (4)
SOLIDS CONCENTRATION, wt pct								
NH <sub>4</sub> <sup>+</sup> .....	0.01	0.08	0.12	0.29	<0.01	0.11	<0.01	<0.01
Br <sup>-</sup> .....	.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Cl <sup>-</sup> .....	.005	.26	.27	.36	.15	1.32	.44	.87
CO <sub>3</sub> <sup>2-</sup> .....	.01	13.1	23.6	8.10	<.01	<.01	<.01	<.01
F <sup>-</sup> .....	.001	.09	.06	.14	.08	.05	.007	.16
NO <sub>3</sub> <sup>-</sup> .....	.01	<.01	<.01	<.01	<.01	<.01	.011	<.01
PO <sub>4</sub> <sup>3-</sup> .....	.002	.10	.108	.15	.26	.25	.008	<.002
SO <sub>4</sub> <sup>2-</sup> .....	.002	.23	.26	.33	7.03	.09	.011	.004
LIQUIDS CONCENTRATION, µg/mL								
NH <sub>4</sub> <sup>+</sup> .....	0.2	850	1,500	590	<0.2	19	NAp	NAp
Br <sup>-</sup> .....	1.5	<1.5	<1.5	<1.5	<1.5	<1.5	NAp	NAp
Cl <sup>-</sup> .....	.1	6.6	13	1,200	76	1,300	NAp	NAp
CO <sub>3</sub> <sup>2-</sup> .....	100	<100	<100	<100	<100	<100	NAp	NAp
F <sup>-</sup> .....	.05	<.02	<.02	1.75	<.02	20	NAp	NAp
NO <sub>3</sub> <sup>-</sup> .....	.5	1.4	2.5	<.5	<.5	7.2	NAp	NAp
PO <sub>4</sub> <sup>3-</sup> .....	.5	<.5	<.5	<.5	<.5	<.5	NAp	NAp
SO <sub>4</sub> <sup>2-</sup> .....	1.0	8.7	21	430	3.4	<1.0	NAp	NAp
pH .....	NAp	9.5	9.6	9.0	6.5	6.5	NAp	NAp

NAp Not applicable.

<sup>1</sup> Results below these limits are reported as less than (<) the limits. Limits are based on 0.2 g in 100 mL for solids.**Table 18.—Elemental analytical results for tailings liquids from laboratory and pilot-plant leach processes, micrograms per milliliter**

Element	Analysis working limits <sup>1</sup>	Process and number of replicates					Element	Analysis working limits <sup>1</sup>	Process and number of replicates				
		GRAML (5)	CuAmL-Lb (6)	CuAmL-Pp (5)	HTPSAL (6)	RHCIAL (6)			GRAML (5)	CuAmL-Lb (6)	CuAmL-Pp (5)	HTPSAL (6)	RHCIAL (6)
Ag .....	0.03	<0.03	<0.03	<0.03	<0.03	<0.03	Mg .....	0.003	3.7	4.6	3.2	6.5	14.8
Al .....	1.5	<1.5	<1.5	<1.5	<1.5	<1.5	Mn .....	.03	.06	.08	<.03	145	39.9
As .....	.003	.046	.005	.018	<.003	<.003	Mo .....	1.0	2.3	<1.0	30	<1.0	<1.0
Ba .....	.6	<.6	<.6	<.6	<.6	27.6	Na .....	.006	26	34	1,250	135	15.7
Be .....	.04	<.04	<.04	<.04	<.04	<.04	Ni .....	.05	<.05	<.05	<.05	56	9.56
Ca .....	.05	.24	.16	2.7	525	6.66	Pb .....	.2	<.2	<.2	<.2	<.2	<.2
Cd .....	.05	<.05	<.05	<.05	.14	<.05	Sb .....	.003	.004	<.003	.007	<.003	<.003
Co .....	.1	<.5	<.5	<.5	5.8	.24	Se .....	.003	<.003	<.004	.02	<.003	<.003
Cr .....	.3	<.3	<.3	<.3	<.2	<.2	Si .....	4.0	9.4	<4.0	22.4	<4.0	<4.0
Cu .....	.03	.37	1.2	<.03	1.2	.16	Ti .....	5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Fe .....	.08	<.08	<.08	<.08	<.08	.21	Tl .....	.3	<.3	<.3	<.3	<.3	<.3
K .....	.03	83	2.1	182	<.03	8.80	V .....	1.3	<1.3	<1.3	<1.3	<1.3	<1.3
Li .....	.03	.10	.15	.23	1.05	<.03	Zn .....	.02	<.02	<.02	<.02	<.5	.15

<sup>1</sup> Results below these limits are reported as less than (<) the limits.**Table 19.—Semiquantitative optical emission spectrograph results on tailings solids and slags from laboratory and pilot-plant leach processes, weight percent**

Element	Detection limit <sup>1</sup>	GRAML	CuAmL-Lb	CuAmL-Pp	HTPSAL	RHCIAL	SmSAL-1	SmSAL-2
B .....	0.002	<0.002	<0.002	<0.002	<0.002	0.002-0.01	0.01-0.1	0.01-0.1
Bi .....	.002	<.002	<.002	<.002	<.002	<.002	<.002	<.002
Ga .....	.001	0.001- .003	0.001- .003	0.001- .003	0.001- .003	.001- .01	<.001	<.001
Nb .....	.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005
Rb .....	.005	.005- .030	.005- .030	.005- .030	.01 - .10	.005	<.005	<.005
Sn .....	.006	<.006	<.006	<.006	<.006	<.006	<.006	<.006
Sr .....	.01	.01 - .10	.01 - .10	<.01	.01 - .10	.01 - .03	<.01	.03- .3
Zr .....	.01	<.01	<.01	.01 - .03	.01 - .03	<.01	<.01	.01- 1

<sup>1</sup> Results below these limits are reported as less than (<) the limits.

ity, and/or EP toxicity as defined in the promulgated regulations (9). Tailings from the tested processes do not exhibit any properties of corrosivity, ignitability, or reactivity as defined, leaving the EP toxicity test as the hazardous waste criteria. Briefly, the EP toxicity test consists of agitating, for 24 h, a minimum sample weight of 100 g of filtered material in 1,600 mL of distilled water

(16:1 liquid-to-solid ratio) to which a maximum of 400 mL of 0.5N acetic acid (4 mL/g of material) may be added to maintain a pH of 5.0±0.2. If all 400 mL of the acid is not required to achieve the desired pH, the remaining volume to make 2,000 mL (20:1 liquid-to-solid ratio) is added as distilled water. The solution is filtered on a 0.45-µm filter. The resulting extract in the EP toxicity test is not to

**Table 20.— EP toxicity test results for tailings and slags from laboratory and pilot-plant leach processes, micrograms per milliliter**

Element	Maximum allowed	GRAML	CuAmL-Lb	CuAmL-Pp	HTPSAL	RHCIAL	SmSAL-1	SmSAL-2
Ag.....	5.0	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
As.....	5.0	.04	<.001	.004	.003	<.001	.002	<.001
Ba.....	100.0	6.0	<1.0	<1.0	<1.0	20	<1.0	2.5
Cd.....	1.0	<.05	<.05	.06	<.05	<.05	<.05	<.05
Cr.....	5.0	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Hg.....	.2	ND	ND	ND	ND	ND	ND	ND
Pb.....	5.0	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Se.....	1.0	<.003	<.003	<.003	<.003	<.003	<.003	<.003

ND Not determined. As reported in references 2 and 3, Hg levels in nodules are extremely low.

exceed 100 times the National Drinking Water Standard for concentrations of eight metals: Ag, As, Ba, Cd, Cr, Hg, Pb, and Se. Table 20 lists these allowed maximum concentrations and the results of duplicate tests. As shown in table 20, no elements were present near the maximum allowable concentration, making these waste materials nonhazardous. Because this is the only criteria for on-land disposal, this would seem to allow routine waste disposal operations to be employed.

### ASTM Shake Extraction Test

A second test, the ASTM shake extraction test (10), has been proposed by ASTM as an alternate method for evaluating wastes. This test consists of contacting a minimum of 350 g of dried material with distilled deionized water at four times the weight of the sample in grams. The slurry is agitated in a sealed container for 48 h and the liquid portion filtered on a 0.45- $\mu$ m filter. The extract is then analyzed for the desired components. In this test, the levels of 17 elements listed at the start of the "Tailings Characterization" section were determined. Results of these analyses are given in table 21. Levels shown in table 21 for these elements are all extremely low, and lower than the results in table 20 for those elements under EP toxicity.

### EPA-COE Seawater Elutriant Test

In the possible case of ocean disposal of nodule tailings by ocean dumping or ocean outfall, the tailings may be subjected to a seawater leachate test. The EPA-COE dredge material elutriant test was used to evaluate the seawater leachable metals in the tailings

**Table 21. — ASTM shake extraction test results for tailings and slags from laboratory and pilot-plant leach processes, micrograms per milliliter**

Element <sup>1</sup>	GRAML	CuAmL-Lb	CuAmL-Pp	HTPSAL	RHCIAL	SmSAL-1	SmSAL-2
Ag.....	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
As.....	.016	<.003	<.003	<.003	<.003	<.003	<.003
Ba.....	<.6	<.6	<.6	<.6	19.6	<.6	<.6
Be.....	<.04	<.04	<.04	<.04	<.04	<.04	<.04
Cd.....	<.02	<.02	<.02	<.02	<.02	<.02	<.02
Co.....	<.1	<.1	<.1	3.2	.24	<.1	<.1
Cr.....	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Cu.....	.53	.16	<.05	.4	.58	<.2	<.05
Fe.....	<.08	<.08	<.08	.52	<.08	<.08	<.08
Mn.....	2.25	.94	<.03	20	1.7	1.4	<.03
Mo.....	<1.0	<1.0	3.8	<1.0	<1.0	<1.0	<1.0
Ni.....	<.05	<.05	<.05	7.0	9.5	<.05	<.05
Pb.....	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Sb.....	<.003	<.003	<.003	<.003	<.003	<.003	<.003
Se.....	<.003	<.003	<.003	<.003	<.003	<.003	<.003
Tl.....	<.3	<.3	<.3	<.3	<.3	<.3	<.3
Zn.....	<.02	.10	<.02	.10	.13	<.02	<.02
Final pH	8.1	8.8	8.4	6.7	5.0	8.8	10.2

<sup>1</sup> Hg not included because of its extremely low levels of occurrence in nodules.

(11). The procedure consists of contacting a weighed volume of material with four times the volume of seawater, agitating for 1 h, filtering, and analyzing the seawater solution. Concentrations are compared to those in the seawater prior to leaching. Based on this analysis, concentrations of the elements at proposed mixing levels found in ocean dumping and ocean outfalls can be extrapolated. Because the types of ocean disposal methods determine the final levels, the ability to safely ocean dump is relevant to the levels required and methods used. Table 22 gives the levels found in the extract and in the seawater prior to leaching.

**Table 22.—EPA-COA seawater elutriant test results for tailings and slags from laboratory and pilot-plant leach processes, micrograms per milliliter**

Element <sup>1</sup>	Seawater	GRAML	CuAmL-Lb	CuAmL-Pp	HTPSAL	RHCIAL	SmSAL-1	SmSAL-2
Ag.....	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
As.....	<.003	<.003	<.003	<.003	<.003	<.003	<.003	<.003
Ba.....	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Be.....	<.07	<.07	<.07	<.07	<.07	<.07	<.07	<.07
Cd.....	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02
Co.....	<.1	.2	.26	<.1	<.1	.14	<.1	<.1
Cr.....	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Cu.....	<.05	.15	.22	<.05	<.15	<.1	.12	<.05
Fe.....	<.08	.20	<.08	<.08	<.10	<.08	<.08	<.08
Mn.....	<.05	1.46	.22	.3	1.28	18.4	12.1	.22
Mo.....	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Ni.....	<.05	.27	.13	<.05	.48	6.2	<.05	<.05
Pb.....	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Sb.....	<.003	<.003	<.003	<.003	<.003	<.003	<.003	<.003
Se.....	<.003	<.003	<.003	<.003	<.003	<.003	<.003	<.003
Tl.....	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3
Zn.....	<.02	<.02	<.02	<.02	<.02	.13	<.02	<.02
Final pH.....	8.5	8.0	8.2	7.9	6.5	5.8	8.5	10.0

<sup>1</sup> Hg not included because of its extremely low levels of occurrence in nodules.

## SUMMARY AND CONCLUSIONS

Laboratory processing and characterizing of manganese nodule tailings and slags from the five proposed first-generation processes have been described. All processes except the reduction and hydrochloric acid leach process are adaptations of currently practiced technology for nickeliferous laterites (15-22). Samples of industrially run pilot-plant tailings were available only for the Cuprion ammoniacal leach process as the remaining industrial concerns considered the tailings' content proprietary.

The five processes that were operated in the laboratory were designed to generate tailings and slags and not to produce final products. Approximately 30 to 40 lb of tailings was produced for each process and about 125 lb of slags. Overall extraction of the value metals of Co, Cu, Ni, and/or Mn were generally greater than 90 pct for Cu, Ni, and Co with lower values for the ammonia gas reduction and ammoniacal leach and Cuprion ammoniacal leach based processes (laboratory and pilot plant) for Co and Cu.

All tailings and slags were analyzed for physical properties (except smelting and sulfuric acid leach), mineral content, elemental and ion content, and leachability using the EP toxicity test (9), the ASTM shake extraction test (10), and The EPA-COE seawater elutriant test (11).

For the ammonia-based processes, the physical properties, mineral content, and elemental and ion content were very similar with no significant variation in composition and physical properties. The high-temperature and high-pressure sulfuric acid leach process tailings physical properties were similar to the ammonia-based processes. The minerals  $Mn_3O_4$  and  $MnO_2$  were identified as minor (10 to 25 wt pct) constituents. Chemical analyses were not significantly different than the ammonia-based processes. All of these processes — ammonia-based and high-temperature and high-pressure sulfuric acid leach — are three-metal recovery schemes and do not recover manganese. With manganese and iron as the major constituents of nodules, the tailings consist

mainly of iron oxide and hydroxides, manganese oxides, and for the ammonia-based processes,  $MnCO_3$ .

The reduction and hydrochloric acid leach process tailings were different than the ammonia-based and high-temperature and high-pressure sulfuric acid leach tailings, being less dense, finer particle size, and devoid of manganese. The primary constituents were iron oxides and hydroxides, quartz, and feldspars. Chemically the tailings were predominately iron, silicon, and aluminum. The levels of Cr and Ni observed in these tailings are high because of corrosion of the Inconel 601 tube used in the reduction and hydrochlorination of the nodules at 500° C.

The slags from the smelting and sulfuric acid leach process were of two types: the smelting slags and the ferromanganese slags. Each slag was analyzed mineralogically and chemically. The smelting slags were predominately  $Mn_2SiO_4$  and were used to produce ferromanganese. The slags from the ferromanganese tests were predominately  $Ca_2SiO_4$  and  $Ca_2Al_2SiO_7$ . Only a limited amount of ferromanganese slags were produced because of equipment problems and time constraints.

The final testing procedure for the tailings and slags was three leachate tests. The EP toxicity test is used to determine whether a waste is hazardous or not. The ASTM shake extraction test is an alternative to the EP toxicity test and was performed for comparison purposes. The EPA-COE seawater elutriant test was used to determine what element might leach in a seawater environment in the case of ocean disposal of nodule tailings. Results obtained in this study show that the tailings and slags produced in the laboratory and the pilot plant are nonhazardous as defined in the EP toxicity test. None of the tailings and slags exceeded the maximum allowable limit for the eight metals in question. Results of the ASTM and EPA-COE tests gave values lower than that of the EP test for the elements in common for the two tests. Overall leachability for the 17 elements analyzed were near or below detection limits.



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